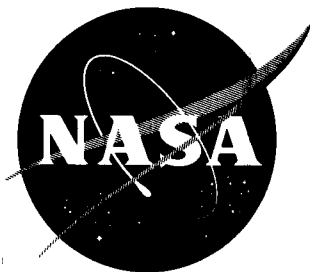


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ULTRAVIOLET PHOTODETECTORS

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ULTRAVIOLET PHOTODETECTORS

by

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SUMMARY

The need for detectors in spectroscopic research in both the laboratory and in space has led in recent years to the development of a variety of spectrally selective detectors which may be put into three broad categories: (1) photoionization chambers having relatively narrow passbands within the region from 1050A to approximately 1500A; (2) multiplier phototubes having high-work-function photocathodes and ultraviolet transmitting windows; and (3) multiplier phototubes having high-work-function cathodes and no windows. This report reviews the characteristics of vacuum ultraviolet ion chambers having fill gases such as nitric oxide, acetone, carbon disulfide, or ethylene oxide with windows of lithium fluoride, cadmium fluoride, or barium fluoride. Their quantum efficiencies range from approximately 0.10 to 0.50 photoelectron/quantum, and the chambers may be operated in a gas multiplication mode with gains of 10^3 at 600 to 800 volts. The characteristics of photomultipliers and phototubes having alkali-tellurium, copper-iodine, or other cathodes with lithium fluoride, sapphire, quartz, or no windows are described. Some of the photomultipliers studied have quantum efficiencies as high as 0.20 photoelectron/quantum and exhibit long-wavelength rejection ratios of many orders of magnitude over only several hundred angstroms.

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INTRODUCTION

A substantial part of the space sciences consists of measurements of astrophysical or geophysical quantities made by means of detectors sensitive to various portions of the ultraviolet wavelength region. The development of observational programs has required considerable extension of the variety of ultraviolet detectors available for scientific use. At the Stockholm meeting of the International Commission for Optics in 1959, characteristics of middle ultraviolet detectors (3000A to 2000A) investigated during the preceding 10 years were presented. Spectral response curves of typical examples of these detectors are given in Figure 1 which is taken from Reference 1. Additional information on the techniques of middle ultraviolet detection is given by Dunkelman, Fowler, and Hennes (Reference 6).

In the past three years the continuing need for detectors in observational programs in astrophysics and planetary optics has necessitated increased efforts in the development of ultraviolet detectors.

These spectrally selective detectors may be put in three broad categories; (1) photoionization chambers having relatively narrow passbands within the region from 1050A to approximately 1500A; (2) multiplier phototubes having high-work-function photocathodes and ultraviolet transmitting windows; and (3) multiplier phototubes having high-work-function cathodes and no windows. Both the measurements and the detectors described in the first category have been made primarily at GSFC. The measurements described in the second category have been made at GSFC on detectors prepared for GSFC by industrial or governmental research and development laboratories. The measurements described in the third category have been made partly at GSFC and partly at other governmental or industrial laboratories.

PHOTOIONIZATION DETECTORS

Photoionization chambers can be filled with gases whose ionization potential is of interest for use in a variety of applications in the space sciences. In the papers on Photon-Gas Cross Sections of the First International Conference on Vacuum Ultraviolet Radiation Physics, the subject was reviewed by Ditchburn (Reference 7), Watanabe (Reference 8), Weissler (Reference 9), and Vodar (Reference 10).

*Presented at the First International Conference on Vacuum Ultraviolet Radiation Physics, University of Southern California, April 16-19, 1962; and published in *J. Quant. Spectr. and Radiative Transfer* 2:533-544, October/December 1962.

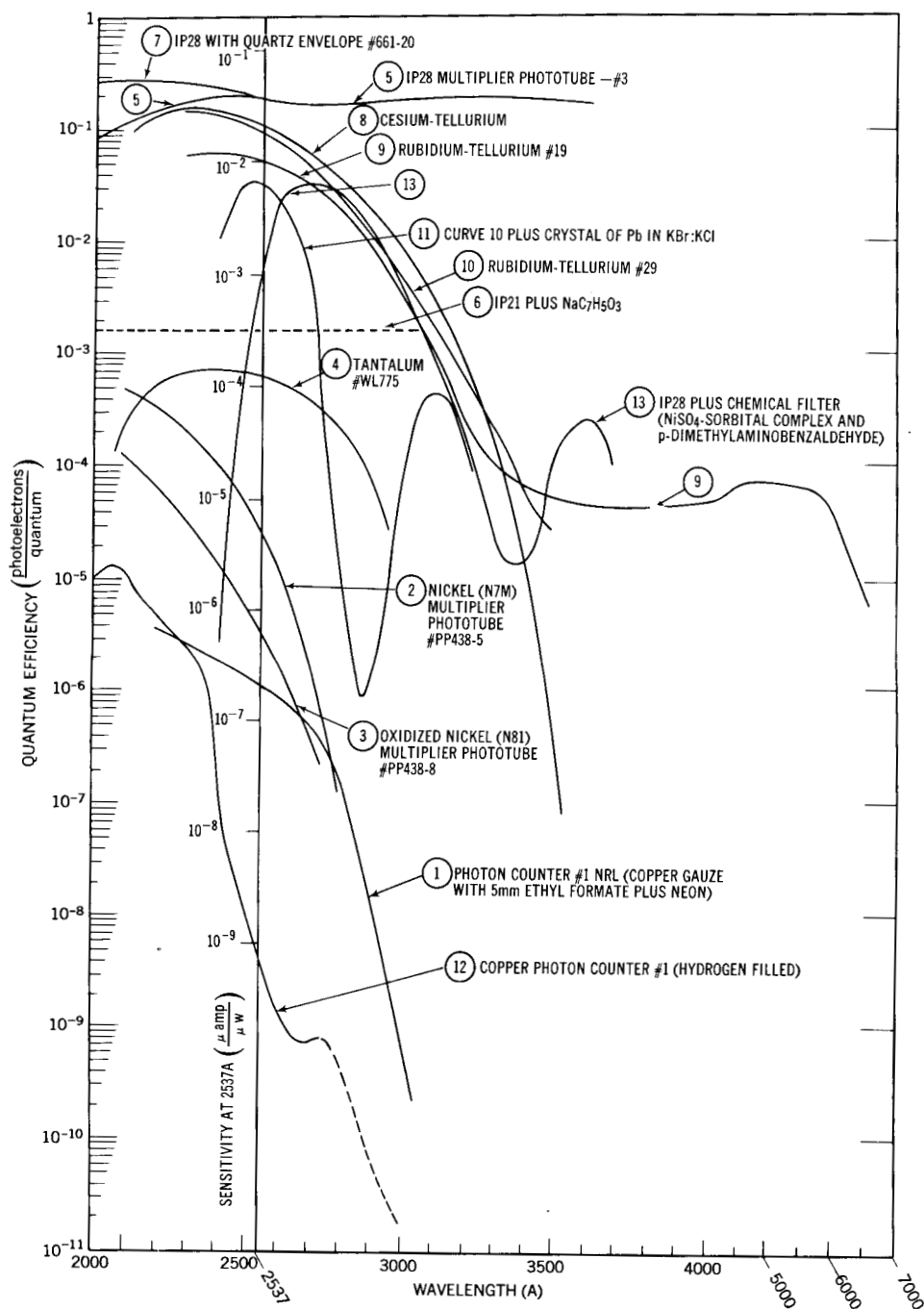


Figure 1—Spectral response curves (quantum efficiencies) for some typical middle ultraviolet detectors. Curves 1, 9, 10, 11, and 12 are unpublished measurements by L. Dunkelman while at the Naval Research Laboratory, Washington, D. C. Curves 2 and 3 are from Reference 2, curve 4 from a Westinghouse Specification, and 5 and 7 from Reference 3. Curve 6 is shown for comparison of the typical overall quantum efficiency of sodium salicylate coated on a 1P21 photomultiplier. This yield is small; however, by using a high-yield end-window Cs-Sb type photomultiplier and optimizing coating thickness, overall efficiencies of about 5×10^{-2} photoelectrons/quantum may be obtained. Curve 8 is from Reference 4. Curves 9 and 10 were obtained with an opaque cathode in a phototube of 9741 Corning glass; curve 9 shows the long-wavelength sensitivity of a phototube having excess rubidium. Curve 13 gives the response of the Cs-Sb surface of the 1P28 photomultiplier modified by a combination chemical filter to produce a convenient passband (see also Reference 5).

The effort at GSFC has been a continuation of the investigation and development of ion chambers first used in a series of rocket measurements at the Naval Research Laboratory in the last decade and described by Chubb and Friedman (Reference 11) Byram, Chubb, et al. (Reference 12), and Friedman (Reference 13).

From the experience gained with these early detectors a somewhat newer design was developed at GSFC and reported by Stober (Reference 14) and Stober, Scolnik, and Hennes (Reference 15). This type of ion chamber (Figure 2) consists of a small ceramic shell, gold plated on the inside, fitted with a central collecting wire electrode and employing a window of suitable transmittance characteristics to limit the short wavelength response. A completed crystal-window chamber is shown in the center of the figure. At the right is a chamber in which a thin metal window, such as aluminum or beryllium, is used, with the supporting grids, for ion chamber detection in the soft x-ray region.

The most desirable features of these ion chambers are: (1) extremely high spectral selectivity, (2) high quantum efficiency, (3) ruggedness and compactness, (4) low electrical leakage, and (5) good vacuum seal properties. Figure 3 shows a section of the ion chamber. The shell of alumina ceramic was made for GSFC by the Coors Porcelain Company;* its interior has several layers of metallic deposits, the outermost (surface) layer being a gold plating. Around the central pin collector electrode where it passes through the shell is an electrical guard ring which is normally kept at ground potential. The window is held onto a gold plated silver flange by several coats of one of the Hysol epoxies. The flange is in turn fastened to the metal plated ceramic shell by soft solder. Window materials of LiF , CaF_2 , and BaF_2 cleaved crystals have been used, as well as the thin beryllium and aluminum foils mentioned. An extensive collection of the transmission properties of a number of solid and gaseous materials has been published by Bryam, Chubb, et al. (Reference 12).

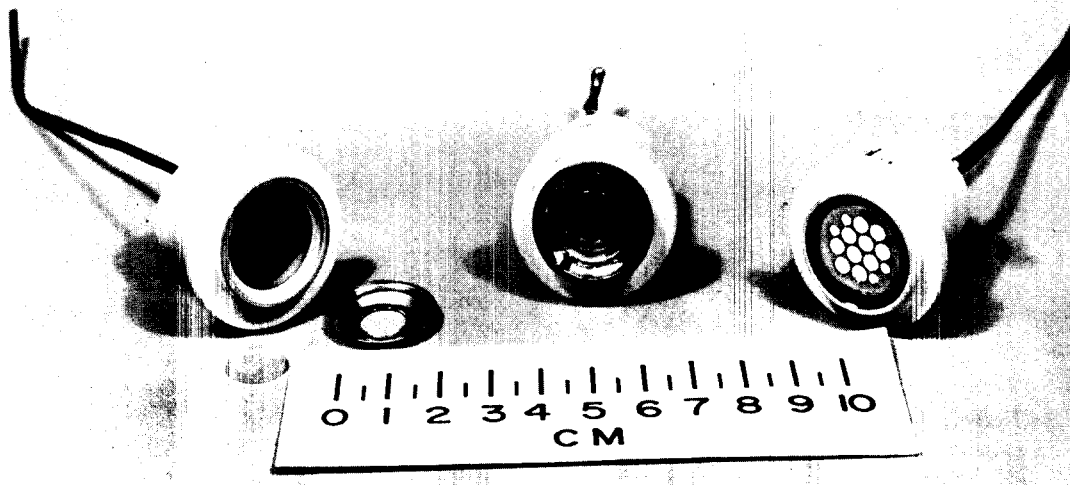


Figure 2—Three NASA ceramic ion chambers. Left, an unfinished chamber with a LiF crystal window and a gold plated window flange lying in front of the ceramic shell. Center, a completed ion chamber. Right, a chamber with an aluminum window, for use in the soft x-ray region.

*Coors Porcelain Company, Golden, Colorado.

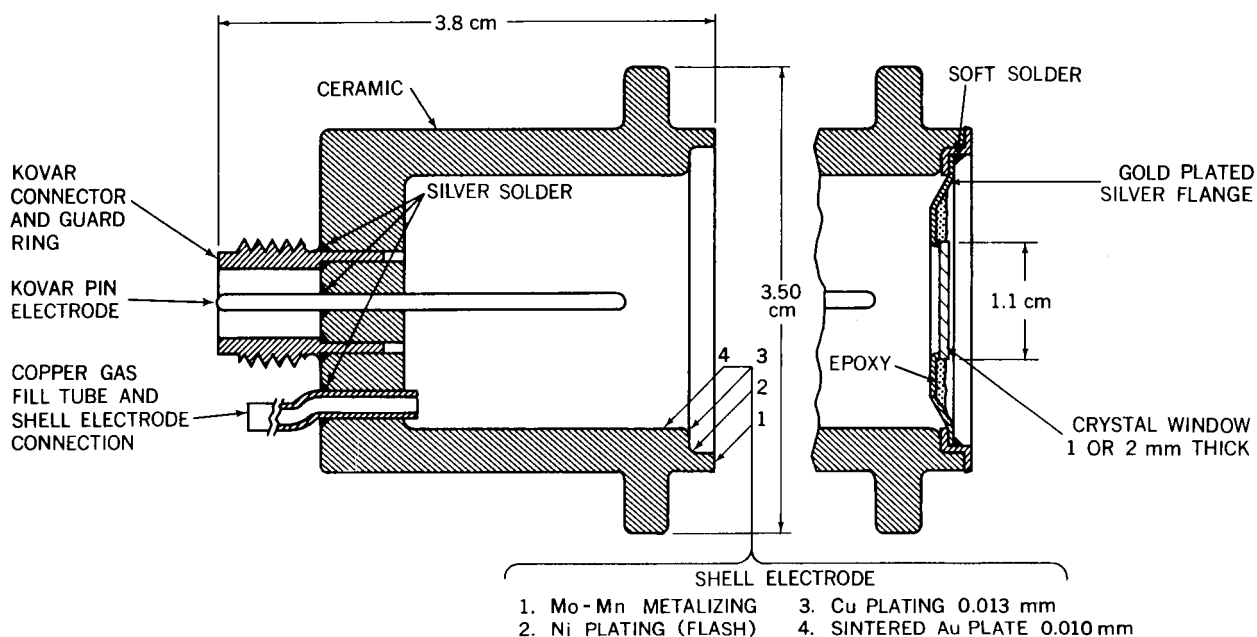


Figure 3—Cross section of an alumina ceramic metal-coated ion chamber.

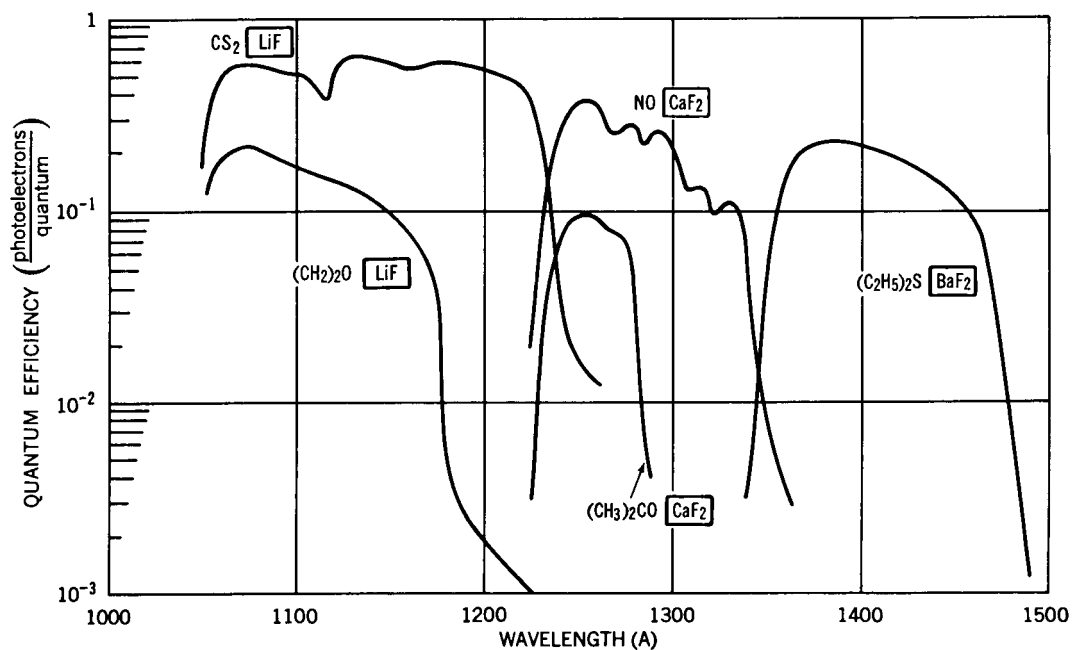


Figure 4—Spectral responses of several ion chambers for the region from 1000A to 1500A. Boxed symbols refer to the phototube window materials. Smoother curves are shown, although a certain amount of fine structure is obscured in this way. Note the high quantum efficiencies and narrow response regions of some of these detectors.

Figure 4 shows the measured yields of five of the filling gas and window material combinations which have been used recently in several series of rocket experiments. Smoothed curves are shown which obscure, in some cases, fine structure in the gas ionization yield curves. Note the high quantum efficiency and narrow response region of, for example, acetone with a CaF_2 window. In measurements of solar flux, or in other situations where there are high fluxes, the ion chambers are used in a non-gas-gain condition. A flat plateau region for ion collection exists when the applied voltage is in the range of 20 to 60 volts. However, in many cases the incident flux is so small—as for example, with stellar fluxes—that the ion chambers are operated at gas gains of the order of 1000. This gain requires 600 to 800 volts, although the steep gain curve makes the response quite sensitive to voltage fluctuations. Table 1 summarizes the most pertinent features of these ion chambers.

Table 1
NASA Ion Chamber Features.

Gas Filling	Chemical Formula	Window Material	Spectral Response (Å)	Quantum Efficiency* (photoelectrons/quantum)
Ethylene oxide	$(\text{CH}_2)_2\text{O}$	LiF	1050-1180	0.10-0.20
Carbon disulfide	CS_2	LiF	1050-1240	0.50-0.60
Acetone	$(\text{CH}_3)_2\text{CO}$	CaF_2	1230-1290	0.08-0.10
Nitric oxide	NO	CaF_2	1230-1350	0.10-0.30
Nitric oxide	NO	LiF	1050-1350	0.10-0.50
Diethyl sulfide	$(\text{C}_2\text{H}_5)_2\text{S}$	BaF_2	1350-1480	0.10-0.25

*Based on a value of 0.81 photoelectrons/quantum for NO at the Lyman-alpha wavelength (1216Å).

PHOTOEMISSIVE DETECTORS

The second category of detector development described in this report is the photoemissive detector. In this area GSFC has worked rather closely with industrial research and development laboratories which have prepared a variety of high-work function photocathodes, both opaque and semi-transparent. The intention has been to develop cathode preparation techniques which lead to laboratory and eventually flight photodiodes, photomultipliers, and image tubes. Until recently the only spectrally selective ultraviolet detectors have been of the pure metal type resulting from the early work of Rentschler, Henry, and Smith (Reference 16), and others who studied tantalum, cadmium, nickel, and other metals in the 2000Å to 3000Å region. Quantum efficiencies in the middle ultraviolet are at best 10^{-3} but more generally 10^{-5} photoelectrons/quantum.

Typical of these pure metals is gold, whose distribution of quantum efficiency has been measured by Childs (Reference 17) and others. Childs found that the quantum efficiency of one photomultiplier at 2000Å was approximately 10^{-3} photoelectrons/quantum. A comparison of his data with Figure 1 of this report shows that the spectral response characteristic of gold is similar to that of nickel except that the gold has a better rejection at the longer wavelengths. Extensive studies of the quantum

efficiencies of metals in the far ultraviolet were made in the early 1950's by Hinteregger and Watanabe (Reference 18) and by Walker, Wainfan, and Weissler (References 19 and 20), and were reviewed later by Weissler (Reference 21).

Also useful has been the well known composite surface, cesium-antimony (Cs-Sb), discovered and studied in 1936 by Görlich (Reference 22), which has enjoyed a deserved reputation as a very efficient visible and near ultraviolet photoemitter. A comprehensive study of the photoelectric effect in alkali-antimony has been made by Spicer (Reference 3). Cesium-antimony has been well developed but the extension of its usefulness towards and into the vacuum ultraviolet has been slow.

Figure 5 includes the spectral distribution of the quantum efficiencies of several photocathode materials in the vacuum and middle ultraviolet regions. The extreme right curve shows the short

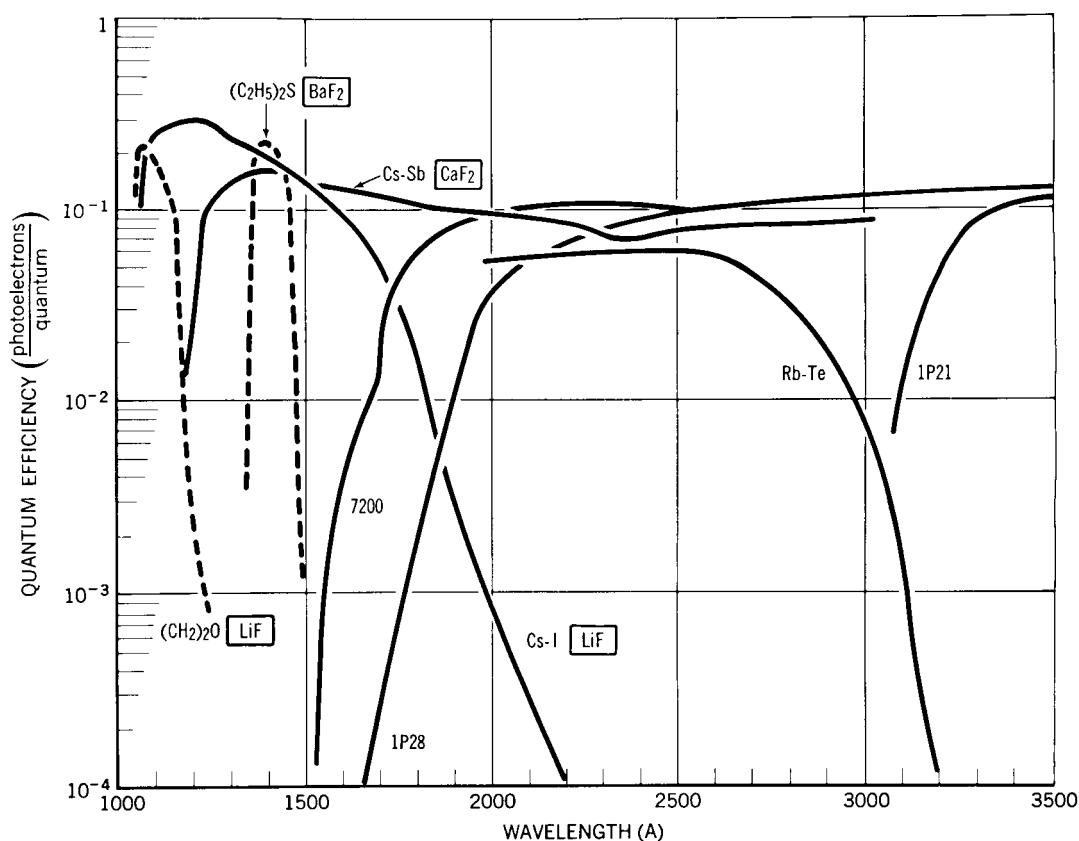


Figure 5—Spectral responses of several photodetectors in the vacuum and middle ultraviolet regions. Boxed symbols refer to the phototube window materials. The 1P21, 1P28, and 7200 curves indicate the responses of a few of many photomultiplier types with Cs-Sb cathodes and envelopes of glass, of Corning 9741, and of fused silica, respectively. The Cs-Sb CaF_2 curve gives the measured response of a photomultiplier with a Cs-Sb photocathode and also a CaF_2 window that extends its response down to 1250 Å. The Rb-Te curve is a typical response of a "solar blind" photocathode. This term refers to the fact that the high-work function photosurface is relatively insensitive to all visible and near ultraviolet wavelengths and therefore to the sun's light as seen through the earth's atmosphere. The Cs-I LiF curve gives the response of a photosurface which rejects a good deal of the middle and near ultraviolet as well as the visible wavelengths. The $(\text{C}_2\text{H}_5)_2\text{S}$ BaF_2 and $(\text{CH}_2)_2\text{O}$ LiF curves show, for comparison, the responses of two photoionization chambers also shown in Figure 4.

wavelength portion of the response of the 1P21, a Cs-Sb photomultiplier which has a glass envelope and is used primarily in the visible region or with phosphors in the vacuum ultraviolet. Another photomultiplier, the 1P28, introduced some 15 years ago, extends the Cs-Sb range just into the beginning of the vacuum ultraviolet by employing an ultraviolet transmitting glass. By using a quartz envelope (Reference 2) with a Cs-Sb photosurface in photomultiplier designated as 7200, the range is extended to approximately 1600Å. Dunkelmann, Fowler, and Hennes (Reference 23) reported on the results obtained with several ultraviolet photodetectors—among them a Cs-Sb photomultiplier having a CaF_2 window. Figure 5 shows the resulting comparatively flat, high quantum efficiency down to 1225Å. Windows of LiF have further extended the sensitivity to 1050Å. It is of interest to note that in 1952 a photocell with a LiF window was prepared by Hinteregger and Watanabe (Reference 18), but it was not until 1957 that a LiF windowed multiplier was reported. At that time Garton, Webb, and Wildy, (Reference 24) used such a photomultiplier having a tungsten cathode.

A most significant advance in selective ultraviolet detection occurred when Taft and Apker (Reference 4) and their colleagues about 10 years ago reported on the distribution of the photoelectric yield of several alkali-tellurium surfaces. Since then Harper and Choyke (Reference 25), Roderick (General Electric Co., private communication), Behring (Reference 26), Kretschmar (private communication and Reference 27), Sowers (Armour Research Foundation, private communication); Sowers, McBride, and Ogan (Reference 28) Linden (CBS Laboratories, private communication), Essig (ITT Laboratories, private communication), Sommer (Reference 29), Causse (Reference 30) and Causse, Dunkelmann, and Hennes (Reference 31) have prepared alkali telluride opaque and semitransparent surfaces. In Figure 6 there are shown two groupings of the spectral responses of phototubes with rubidium-tellurium (Rb-Te) opaque cathodes. The curves numbered 4 and 5 represent the average of the extreme of many tubes prepared by Roderick which were examined several years ago. Note the high efficiencies of these opaque cathodes at 2500Å. The opaque surfaces prepared by Kretschmar

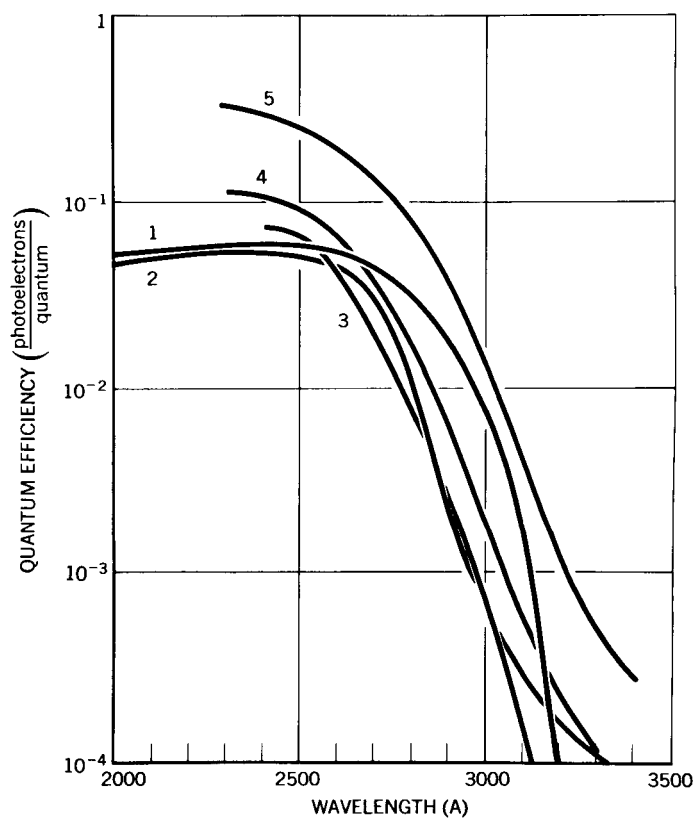


Figure 6—Spectral response curves of Rb-Te opaque-cathode photodiodes showing various degrees of spectral selectivity and quantum efficiency. Curves 1 and 2 refer to diodes made by Kretschmar at the Naval Ordnance Laboratory, Corona, California (Reference 27); and curve 3 refers to the diode made by Kretschmar at the Naval Ordnance Test Station, China Lake, California (private communication). Curves 4 and 5 represent diodes made by Roderick at the General Electric Company (private communication).

(curves 1, 2, and 3), while exhibiting lower yields, provide higher selectivity. This may be due to little or no excess rubidium, and thus appears to be consistent with the early work of Taft and Apker who found that excess cesium produced the impurity-type yield at low photon energies, causing a response tail to extend beyond 3200Å. Figure 7 shows a comparison of spectral response curves of a variety of phototubes containing cesium-tellurium (Cs-Te) photocathodes. No major differences between Rb-Te and Cs-Te with respect to either quantum efficiencies or rejection ratios have been found. The curves marked FW 157-1 and FW 140-12 show the spectral response of photodiodes with opaque cathodes and sapphire windows. The curve marked S.883 refers to the response of a 13-stage experimental photomultiplier with an opaque cathode and a LiF window made by Sommers at RCA (Reference 29). A quantum efficiency of better than 10 percent is achieved with these opaque cathodes, whereas in the case of semitransparent cathodes (curves marked 151 and 152) the efficiencies are appreciably lower. However, a semitransparent cathode just behind the front window results in far better optical coupling than is possible in recessed opaque cathodes. This is frequently an important consideration in application.

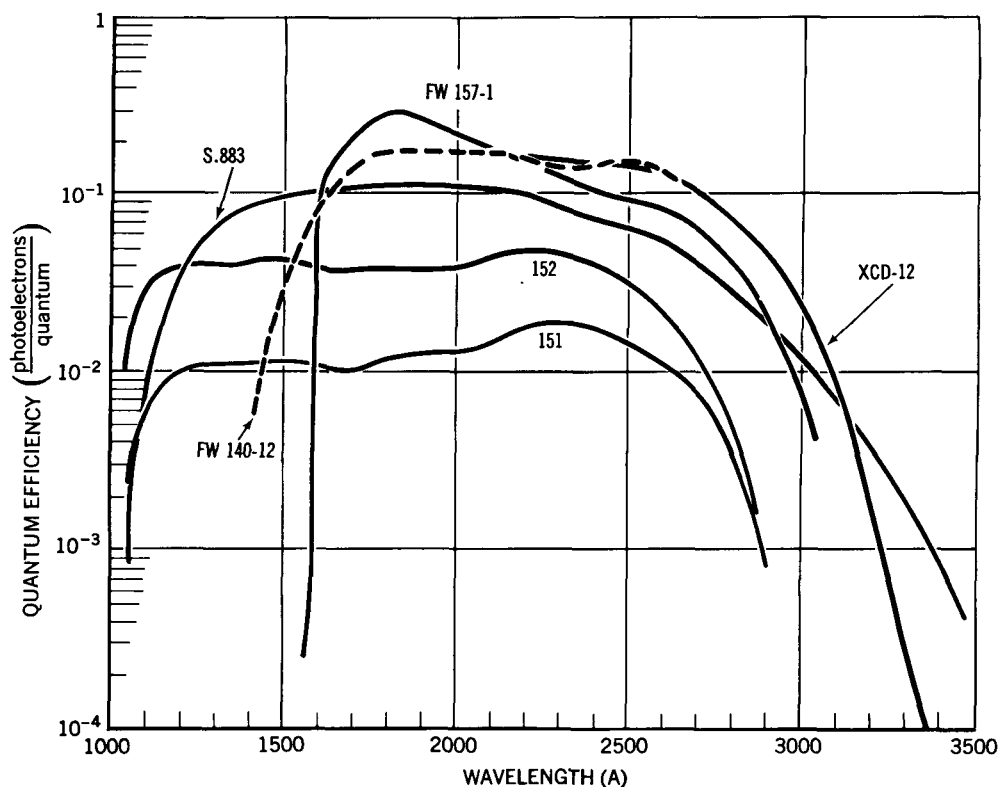


Figure 7—Spectral response curves of Cs-Te phototubes. The 151 and 152 curves refer to 14-stage photomultipliers with semitransparent photocathodes and LiF windows manufactured by ASCOP Division of Electro-Mechanical Research, Inc. The S.883 curve refers to a 13-stage experimental photomultiplier with an opaque cathode and a LiF window made by Sommers at RCA. The other curves refer to opaque-cathode photodiodes made by ITT Laboratories: FW 140-12 and XCD-12, with sapphire windows; and 157-1, with a fused silica window.

Two developments in photoemissive photodetectors have been reviewed thus far. One is the extension of available photocathodes in the ultraviolet merely by the use of appropriate windows which serve to broaden the inherent useful response. This wider spectral response may be very desirable in some applications, especially with dispersive optics. The second development, the use of photoemitters spectrally selective to the ultraviolet, such as the high-work function alkali tellurides, is useful in applications where discrimination against the longer wavelengths is an overriding consideration. Figure 8 is a compilation of the yields of some still higher work function materials which are, in general, spectrally selective to the vacuum ultraviolet region. Curve 6 is taken from the early work by Philipp and Taft (Reference 32) who studied cesium-iodine (Cs-I). Curve 3 represents our recent measurements (Reference 23) of the spectral distribution of the quantum efficiency from a phototube with a Cs-I cathode prepared by Sommer of RCA. Here the photocathode is deposited on a conducting substrate of thin tungsten immediately behind the LiF window; this makes possible, again, convenient end-on coupling. Curves 3 and 6 are quite similar. The slightly lower yield (curve 3) at wavelengths greater than 1400A might be attributable to a transmittance loss in the tungsten conducting substrate, or to excessive thickness of Cs-I. Curves 1, 2, and 5 [potassium-bromine (K-Br), cesium-bromine (Cs-Br), and rubidium-iodine (Rb-I), respectively], from Reference 33, are shown here for comparison and for suggestions of surfaces which should be considered if shorter wavelength cutoffs are of interest. Curve 4, copper-iodine (Cu-I) is discussed along with the curves of Figure 9.

In Figure 9, the scales have been changed in order that 9 orders of magnitude may be displayed. Curve 1 is the familiar Cs-Sb surface. Curve 2 is the Cs-I surface already discussed (curve 3 of Figure 8). Here it can be seen that at 2537A the absolute yield of the Cs-I surface is only 7×10^{-6} . This, as well as the quantum efficiency at 2537A of other cathodes investigated at GSFC, was measured in a calibrated low-pressure mercury arc described by Childs (Reference 35). Curve 3 is a result of recent GSFC measurements of a Cu-I semitransparent surface on tungsten deposited on a LiF window in a phototube which was prepared by Sommer of RCA. This response is similar to that of his Cs-I tube, curve 2, except for the much improved long wavelength rejection ratio which is at least 7

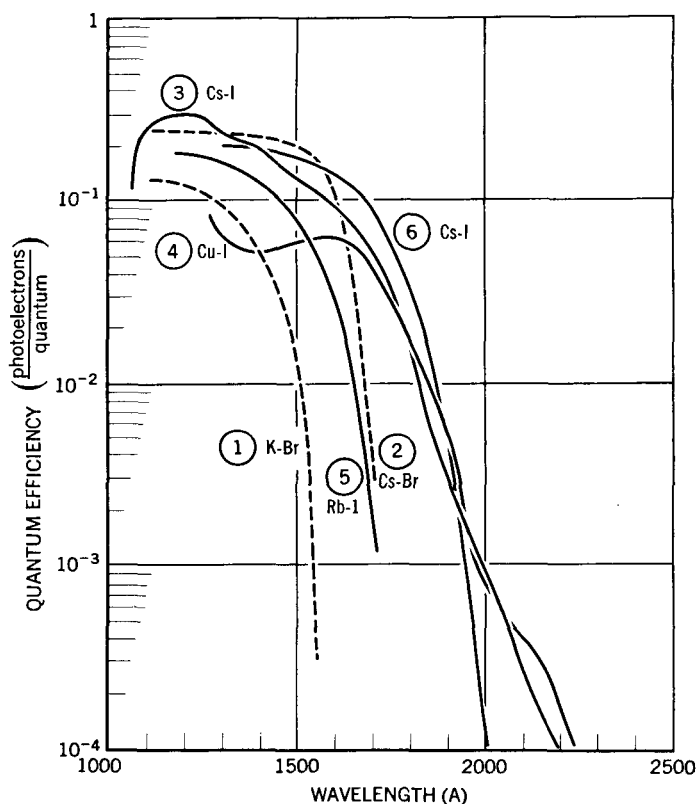


Figure 8—Spectral response curves of several high-work function photocathodes. The K-Br, Cs-Br, and Rb-I curves are taken from Reference 33, the Cs-I curve from Reference 23. The Cu-I is estimated from work presented in Reference 34. The Cs-I curve, given for comparison, is from the work of Reference 32.

orders of magnitude between 1849A and 2537A. The upper limit of the quantum efficiency at the latter wavelength is less than 10^{-9} . The quantum efficiencies at short wavelengths displayed in curves 2 and 3 represent preliminary measurements made at GSFC. In general a peak efficiency of about 0.20 photoelectrons/quantum Lyman alpha (1216A) can be expected for Cs-I with the efficiency of Cu-I being 3 to 5 times less. The dashed portions represent estimated yields interpolated between the measured values at 2000A and 2537A. We can compare these measurements with the results reported in 1960 by Shuba and Smirnova (Reference 34) who established a quantum efficiency of 10^{-1} at the short wavelengths but only a 6 order of magnitude rejection ratio. In 1957, Turner of Imperial College reported (Reference 36) a Cu-I photoemitter with a cutoff at 2300A (although he did not define cutoff) and a peak yield somewhere between 10^{-2} and unity. Additional surfaces of Cu-I recently prepared by Sommer of RCA and Stober at GSFC have been found to remain fairly stable after exposure to air.

WINDOWLESS DETECTORS

The investigation of Cu-I at wavelengths below 1100A is being made with the aid of a Bendix-resistance-strip magnetic photomultiplier, developed by Goodrich and Wiley (Reference 39) and first

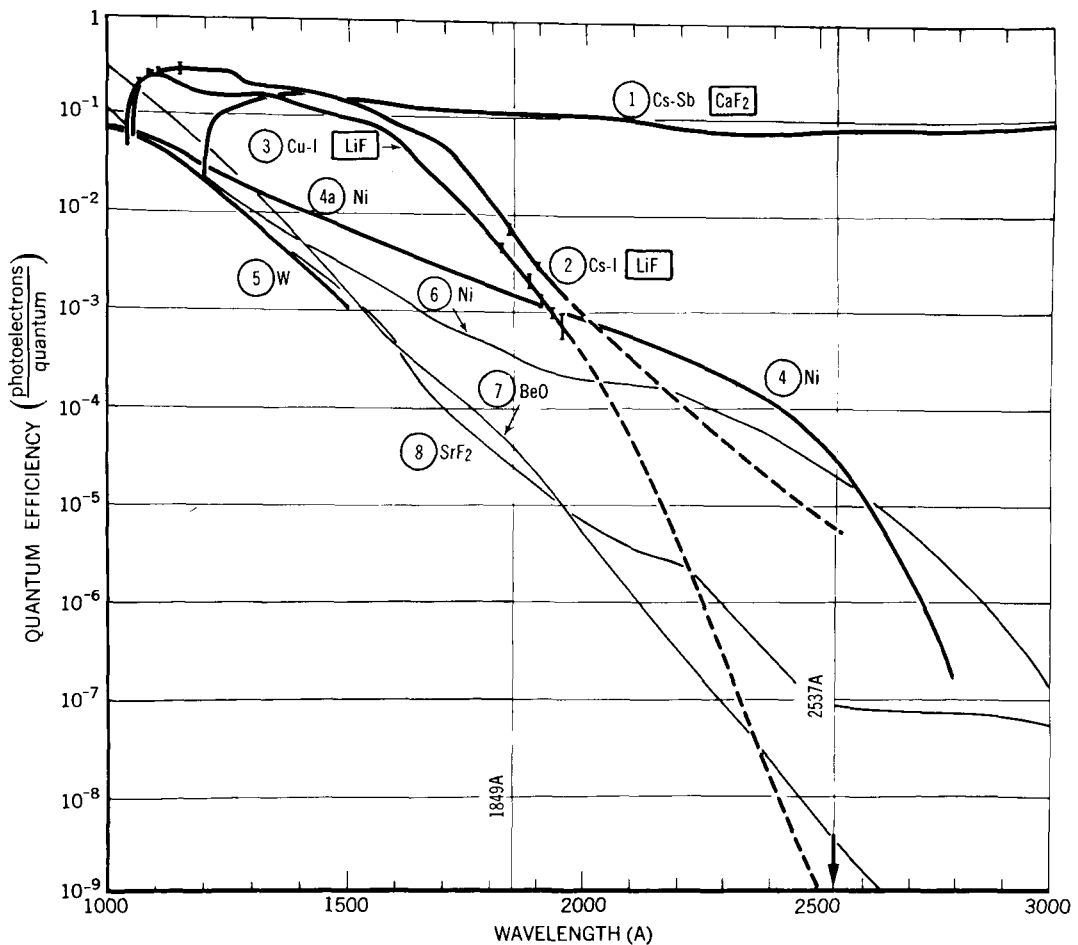


Figure 9—Spectral responses of various photocathodes showing the high sensitivity and excellent long wavelength rejection possible with the high work function materials. Curves 1, 2, and 3 are measurements reported in Reference 23; curve 4 is from Reference 37; and curves 4a and 5 are from Reference 18. Curves 6, 7, and 8, shown for comparison, are from Reference 38.

used by Heroux and Hinteregger (Reference 40) in the late 1950's. Soon after NASA was established it was apparent that smaller versions of the resistance-strip photomultiplier would be needed for the continued observation from rockets and satellites of solar emission in the very extreme ultraviolet. Work was initiated and the middle-sized detector (type M306) shown in Figure 10 was developed. This photomultiplier was reported by Goodrich and Wiley (private communication) to be very quiet, with a dark current, referred to a tungsten cathode, as low as of the order of 1 electron/minute. The multiplier has been successfully employed in the soft x-ray spectrometer to study the solar spectrum in the 10A to 400A region. The instrument was first used in an Aerobee rocket launched on September 30, 1961, as described by Behring, Neupert, and Nichols (Reference 41) and then used in the Orbiting Solar Observatory launched March 7, 1962, as described by Behring, Neupert, and Lindsay (Reference 42). Some results and a preliminary interpretation of the solar observations taken with this soft x-ray spectrometer are given by Neupert and Behring in Reference 43. Other investigators have been working with the windowless electron multiplier developed and investigated by Allen (References 44 and 45).

Another significant design in windowless and small multiplier phototubes is the continuous channel multiplier developed by Goodrich and Wiley (Reference 46) and shown in Figure 11. Briefly, this

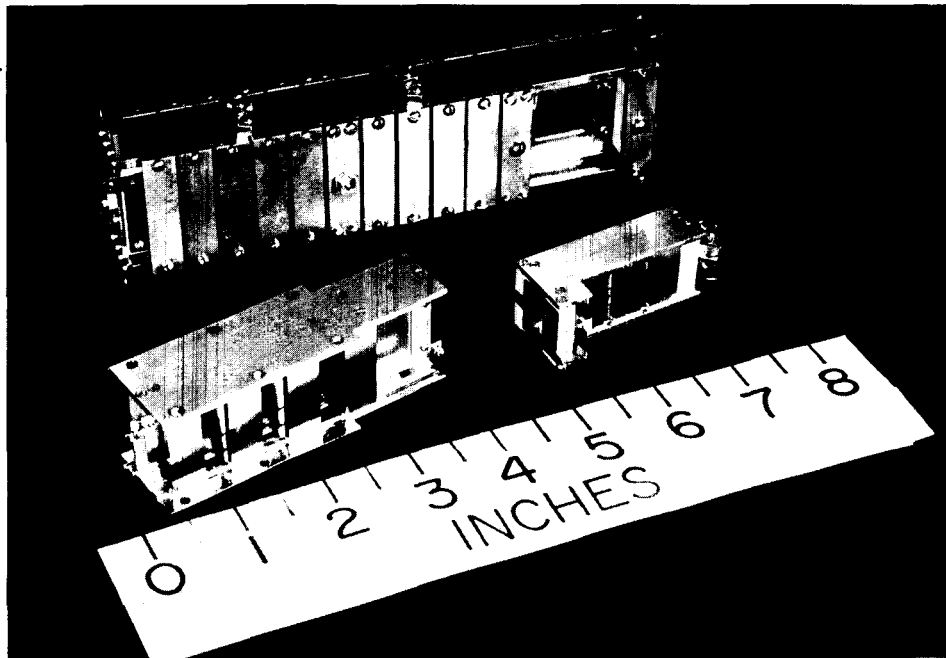


Figure 10—Bendix-resistance-strip magnetic photomultipliers.

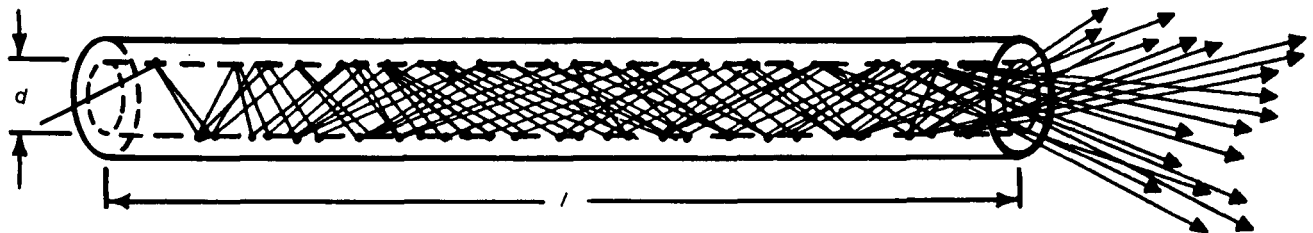


Figure 11—Bendix channel photomultiplier.

Bendix channel multiplier is in the form of a hollow glass tube with a highly resistive inner surface. It has an internal bore diameter of several tenths of a millimeter and has a length to bore diameter ratio (l/d) of approximately 50. A potential difference of 1000 to 2000 volts is maintained between the ends, causing a current on the inner surface; thus, a uniform axial electric field is established down the length of the tube. An initial electron is generated from the inner surface near the open input end. This first electron may be a photoelectron caused by an ultraviolet photon striking the surface, by a photoelectron emitted from the external photocathode, or by any other particle with sufficient energy to cause secondary emission. The emitted electrons cascade down the length of the tube, producing gains of 10^5 or more.

The channel multiplier has been further developed in cooperation with GSFC because of its potential for both laboratory and space applications. Hunter (Reference 47) has recently investigated the channel multiplier and determined that its spectral response is similar to that of tungsten, although the highly resistive inner surface (which is also the photoemitting surface) on the inside of the tube is not tungsten. This type of multiplier will be used in a forthcoming Naval Research Laboratory experiment as described by Angel, Copper, et al. (Reference 48) on the next Orbiting Solar Observatory to study the solar disk at several extreme ultraviolet wavelengths. This type of multiplier has also been under study for other applications such as in an array whose photocathode end is aligned to conform with the exit slit of a spectrometer. Consideration has also been given to employing this detector in an image intensifier which would be useful in nuclear track imaging as well as in other fields.

CONCLUDING REMARKS

In conclusion it should be pointed out that, in this short review, the discussion has been mostly confined to work that has been done either at GSFC or in association with it and which has appeared fruitful for astrophysical and geophysical programs. No attempt has been made here to review the many other areas of photodetector investigation. It is hoped that current researches, such as those described by Hartman (Reference 49) and Walker and Weissler (Reference 50) will soon lead to further advances in photodetection techniques.

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It is a pleasure to acknowledge the work of my colleagues, J. P. Hennes, W. B. Fowler, R. Main, and R. Scolnik, who have participated in making many of the measurements reported here.

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